

# Comment on: “Static correlations functions and domain walls in glass-forming liquids: The case of a sandwich geometry” [J. Chem. Phys. 138, 12A509 (2013)]

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In this Comment, we argue that the behavior of the overlap functions reported in the commented paper can be fully understood in terms of the physics of simple liquids in contact with disordered substrates, without appealing to any particular glassy phenomenology. This suggestion is further supported by an analytic study of the one-dimensional Ising model provided as Supplementary Material.

In a recent paper,<sup>1</sup> Gradenigo et al. have reported on a computer simulation study of a glass-forming liquid constrained by amorphous boundary conditions representative of its equilibrium bulk configurations. This setup has been put forward a few years ago as a possible tool to probe the existence of nontrivial static correlations in bulk glassy systems, through the investigation of point-to-set correlation functions such as configurational overlaps.<sup>2,3</sup> Accordingly, quantities of this type are reported in Ref. 1 for two related geometries, a semi-infinite fluid in contact with a single wall (wall geometry) and a fluid slab sandwiched between two parallel walls (slit geometry). These data are then analyzed in terms of the interplay between the boundary conditions and the complex coarse-grained free-energy landscape postulated by the random first-order transition (RFOT) theory for bulk glassy liquids.<sup>2,4,5</sup>

However, it was recently observed<sup>6</sup> that, outside the realm of glassy physics, constrained systems such as those of Ref. 1 are just special instances of a generic model for fluids in contact with random substrates previously studied with standard tools of the theory of simple liquids.<sup>7</sup> In this framework, it is customary to quantify the direct influence of the quenched-disordered solid boundary on the microscopic fluid configurations via the so-called blocking or disconnected two-point density correlation function, i.e., the covariance of the random density profile established in the presence of the amorphous surface. This correlation function can be straightforwardly turned into configurational overlaps that are analogues of those measured in Ref. 1 and not necessarily bound to be featureless objects, even in the absence of specific glassy features.<sup>6,8</sup>

From this observation, the question naturally arises, whether one really needs to appeal to any particular glassy phenomenology to interpret the behavior of the overlap functions reported in Ref. 1. This is the point addressed in this Comment, through a direct comparison between the wall and slit geometries. For reference, it should be recalled that, in a RFOT-inspired analysis, the two geometries are expected to be ruled by different physics, resulting in well distinct characteristic lengthscales,<sup>4,5</sup> and this is how the data are described in Ref. 1.

The present discussion is guided by an asymptotic result derived in Ref. 6 for the disconnected total correlation function of a nonglassy liquid,  $h_{\text{dis}}(\mathbf{x}, \mathbf{y})$ , when at least one of the points  $\mathbf{x}$  or  $\mathbf{y}$  is far enough from any amorphous boundary. Indeed, one then gets

$$h_{\text{dis}}(\mathbf{x}, \mathbf{y}) \simeq \rho \int d\mathbf{u} h(|\mathbf{x} - \mathbf{u}|) \chi(\mathbf{u}) h(|\mathbf{u} - \mathbf{y}|), \quad (1)$$

with  $\rho$  the number density of the fluid,  $h(r)$  its total correlation function in the bulk, and  $\chi(\mathbf{r})$  the indicator function of the domain from which the fluid particles are excluded by the amorphous boundaries.

The linearity of this equation with respect to  $\chi(\mathbf{r})$  suggests to investigate the range of validity of a simple superposition approximation, in which, for the geometries considered here, the effect on the fluid of the two walls in the slit geometry would merely be the sum of the effects of the two walls taken individually. Note that such a linear regime can be expected on general grounds and that Eq. (1), which represents the leading asymptotic contribution to it, only plays the role of a formal proof of existence. In terms of the configurational overlaps reported in Ref. 1, such a superposition approximation leads to the compact relation

$$q_c(d) - q_0 \simeq 2[q(d) - q_0], \quad (2)$$

with  $q_c(d)$  the overlap at the central plane of a slit of width  $2d$ ,  $q(d)$  the overlap at a distance  $d$  from a single wall, and  $q_0$  the trivial ideal-gas contribution to these functions.

Equation (2) is tested at four temperatures in Fig. 1, where the data of Ref. 1 are plotted accordingly. It appears quite reasonable at all temperatures for  $d \gtrsim 1$  and, in this domain,  $2[q(d) - q_0]$  and  $q_c(d) - q_0$  can be both described by the same exponential decay. This suggests that, in this regime in both geometries, the behavior of the system is ruled by rather simple amorphous-boundary effects.

Gradenigo et al. have shown that  $2[q(d) - q_0]$  keeps an exponential behavior down to  $d = 0$  at all studied temperatures, while  $q_c(d) - q_0$  remains exponential down to  $d = 0.75$  (the smallest value considered for the slit geometry) at the two highest temperatures and tends to

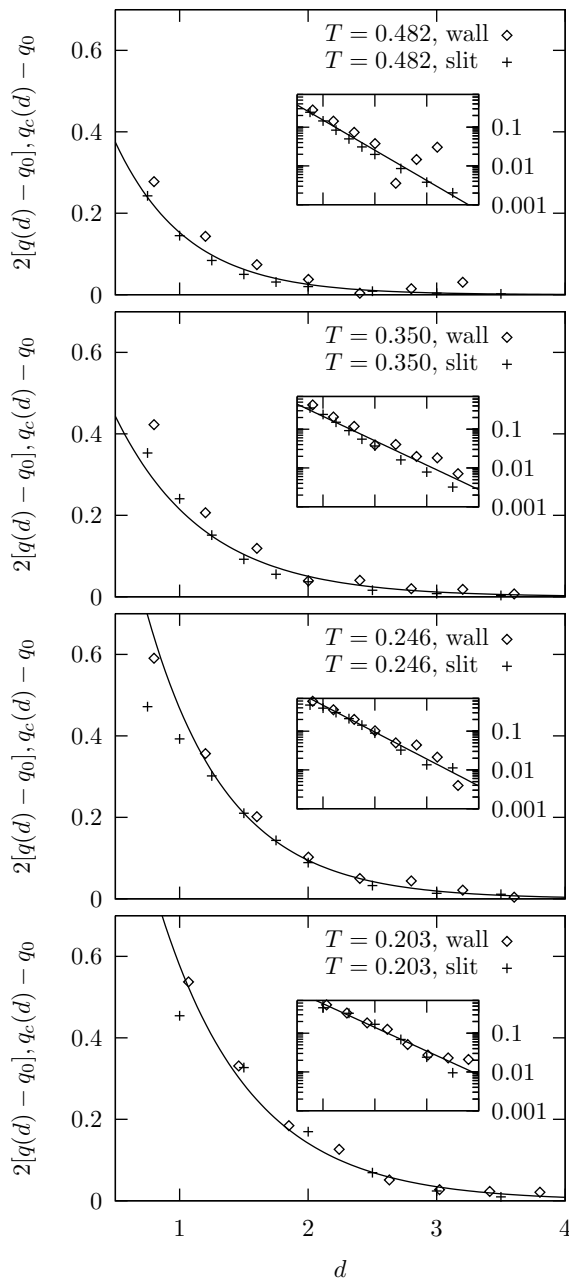


FIG. 1. Comparison at four temperatures of the excess overlap  $q_c(d) - q_0$  at the central plane of a slit of width  $2d$  with twice the excess overlap  $q(d) - q_0$  at a distance  $d$  from a single wall. The continuous lines are joint exponential fits for  $d \geq 1$ . (Insets) Same data in semi-log plots.

flatten for  $d \lesssim 1$  at the two lowest. Such a bending is a foreseeable consequence of the presence of two nearby facing boundaries, i.e., of confinement: For narrow slits, the combined action of the two amorphous walls is indeed expected to restrain the decay of the correlations of the disorder-induced fluid density profile when  $d$  increases more strongly than a mere linear superposition of independent boundary effects. In fact, such a leveling-off disrupting at short distances a medium-to-long-range

exponential decay occurs in models as simple as the one-dimensional Ising model, as shown in the Supplementary Material.<sup>9</sup> If no bending is seen at the highest temperatures, this might only mean that the breadth of the raw confinement effect, expected to decrease as temperature increases, is too small at these temperatures for it to appear in the probed slit-width window.

Therefore, by looking at the data of Ref. 1 from the angle of the physics of simple liquids in contact with disordered substrates, i.e., of raw boundary and confinement effects,<sup>6,7</sup> we do not see any compelling evidence that any specific glassy phenomenology has to be appealed to in order to give an account of the observed behaviors. In particular, in the studied temperature range, there is no obvious sign of distinct and complex physics in the wall and slit geometries, both described by the same simple exponential decay law starting at quite small distances already, at variance with expectations from the RFOT scenario, for instance.<sup>1,4,5</sup>

The contrasting conclusions of Ref. 1 and of this Comment clearly point towards difficulties in the interpretation of measured point-to-set correlation functions. They actually are complex objects, possibly blending ingredients from the physics of normal and glassy liquids that are not easily sorted out.<sup>6</sup> In fact, these difficulties were already acknowledged in Ref. 1, where warnings were raised, based on the experience with an alternative setup, the so-called random pinning geometry.<sup>8,10</sup> However, they could not be made concrete, due to the lack of simple results such as Eq. (1) that appeared more recently.

Finally, it should be mentioned that the predictions of the RFOT theory for the point-to-set correlations are one aspect of an elaborate scenario, also involving features such as a bimodal distribution of overlaps recently observed in computer simulations of spherical cavities.<sup>11</sup> It remains a challenge for the future to find out whether the simple picture put forward in this Comment could also account for these additional aspects.

The authors of Ref. 1 are warmly thanked for sharing their data with us and thus making the present analysis possible.

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- <sup>2</sup>J.-P. Bouchaud and G. Biroli, *J. Chem. Phys.* **121**, 7347 (2004).
- <sup>3</sup>A. Montanari and G. Semerjian, *J. Stat. Phys.* **124**, 103 (2006).
- <sup>4</sup>C. Cammarota, G. Biroli, M. Tarzia, and G. Tarjus, *Phys. Rev. Lett.* **106**, 115705 (2011).
- <sup>5</sup>G. Biroli and C. Cammarota, arXiv:1411.4566 (2014).
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- <sup>7</sup>W. Dong, E. Kierlik, and M. L. Rosinberg, *Phys. Rev. E* **50**, 4750 (1994).
- <sup>8</sup>B. Charbonneau, P. Charbonneau, and G. Tarjus, *J. Chem. Phys.* **138**, 12A515 (2013).
- <sup>9</sup>See supplementary material for an analytic study of the one-dimensional Ising model.
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- <sup>11</sup>L. Berthier, P. Charbonneau, and S. Yaida, *J. Chem. Phys.* **144**, 024501 (2016).
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## Supplementary Material

In this Supplementary Material, we provide and discuss the analytic results for the spin overlap functions of the zero-field one-dimensional Ising model in the “wall” and “slit” geometries. The calculation is a simple exercise in the application of the standard transfer matrix method, whose main elements of solution can be found in the work of Grinstein and Mukamel on a special instance of the random-field Ising model.<sup>12</sup>

*Preliminary.* We consider the standard Ising Hamiltonian for  $N + 1$  spins,

$$\beta H[\mathbf{S}] = -\beta J \sum_{i=0}^{N-1} S_i S_{i+1}, \quad (1)$$

with  $S_i = \pm 1$ ,  $i = 0, 1, \dots, N$ .  $J > 0$  is the exchange constant and  $\beta$  the inverse temperature. For latter use, we define  $\tau = \tanh(\beta J)$ .

Assuming that the spins  $S_0$  and  $S_N$  are frozen, one gets the conditional thermal averages,<sup>12</sup>

$$\langle S_k \rangle_N^{S_0 S_N} = S_0 \frac{\tau^k + S_0 S_N \tau^{N-k}}{1 + S_0 S_N \tau^N}, \quad (2)$$

$$\langle S_k S_l \rangle_N^{S_0 S_N} = \frac{\tau^{l-k} + S_0 S_N \tau^{N-l+k}}{1 + S_0 S_N \tau^N}, \quad k \leq l. \quad (3)$$

*Bulk behavior.* Taking  $N \rightarrow \infty$  and  $0 \ll k \leq l \ll N$ , one gets for the spin correlation function,

$$\langle S_k S_l \rangle_\infty = \tau^{l-k} = e^{(l-k) \ln \tau}. \quad (4)$$

The  $S_0$  and  $S_N$  dependence vanishes as it should, and the bulk correlation length follows as  $\xi_b = -1/\ln \tau$ .

From this correlation function, one can straightforwardly derive the probabilities that two distant spins are parallel or anti-parallel in the bulk,

$$P_{S_k=S_l} = \frac{1 + \tau^{l-k}}{2}, \quad P_{S_k=-S_l} = \frac{1 - \tau^{l-k}}{2}, \quad k \leq l. \quad (5)$$

*“Wall” geometry.* Taking  $N \rightarrow \infty$  and  $k = L \ll N$ , the average magnetization for fixed  $S_0$  reads

$$\langle S_L \rangle_\infty^{S_0} = S_0 \tau^L, \quad (6)$$

independently of  $S_N$ .

Squaring this result and performing a realization average over the value of  $S_0$  (this is needed in principle, but immaterial for this specific calculation), one obtains the spin overlap at a distance  $L$  from the “wall”, i.e., spin 0,

$$Q(L) = \overline{[\langle S_L \rangle_\infty^{S_0}]^2} = \tau^{2L} = e^{-2L/\xi_b}, \quad (7)$$

where  $\overline{\dots}$  denotes the disorder average.

*“Slit” geometry.* Taking  $N = 2L$  and  $k = L$ , the average magnetization for fixed  $S_0$  and  $S_{2L}$  reads

$$\langle S_L \rangle_{2L}^{S_0 S_{2L}} = S_0 \frac{(1 + S_0 S_{2L}) \tau^L}{1 + S_0 S_{2L} \tau^{2L}}. \quad (8)$$

Squaring this result and performing a realization average over the values of  $S_0$  and  $S_{2L}$  with the probabilities  $P_{S_0=S_{2L}}$  and  $P_{S_0=-S_{2L}}$  (this is the condition to have frozen boundaries representative of the equilibrium bulk configurations), one obtains the spin overlap at the center of a “slit” of width  $2L - 1$  delimited by spins 0 and  $2L$ ,

$$Q_c(L) = \overline{[\langle S_L \rangle_{2L}^{S_0 S_{2L}}]^2} = \frac{2\tau^{2L}}{1 + \tau^{2L}} = \frac{2e^{-2L/\xi_b}}{1 + e^{-2L/\xi_b}}. \quad (9)$$

*Discussion.* The one-dimensional Ising model is a minimalist version of the problem at hand, a caricature, actually. It clearly lacks ingredients that can be expected to play an important role in the fluid-based systems, such as the roughness of the boundaries, which is lost because of both its one-dimensional character and lattice-based structure. An oversimplified form of disorder results, which is of an effectively binary nature and fully encoded in the variable  $S_0 S_N = \pm 1$ . Remarkable properties are observed, such as the perfect scaling behavior with respect to the bulk correlation length  $\xi_b$ , that cannot necessarily be expected from fluid systems at the particle scale. Yet, the model provides an interesting opportunity to demonstrate the effects of the wall and slit constraints on an otherwise almost featureless system.

The spin overlaps  $Q(L)$  and  $Q_c(L)$  are plotted as functions of the scaled distance  $L/\xi_b$  in Fig. 1. They clearly display behaviors in line with the qualitative analysis posited in the Comment for the overlap functions of glass-forming liquids. Indeed, for  $L/\xi_b$  large enough, the asymptotic relations

$$Q_c(L) \simeq 2Q(L) = 2e^{-2L/\xi_b} \quad (10)$$

hold. Moreover,  $Q(L)$  is found to be strictly exponential all the way down to  $L/\xi_b = 0$ , while  $Q_c(L)$  levels off at small  $L/\xi_b$  as a consequence of the confinement effect in narrow slits.

It is also interesting to consider the explicit temperature evolution of  $Q_c(L)$ , whose nonexponential domain has to broaden in absolute units of length as the temperature is lowered, because of the associated growth of  $\xi_b$ . It is reported in Fig. 2, where one can see  $Q_c(L)$  crossing over from an exponential to a nonexponential shape (in the window  $L \geq 2$ , for instance) as the temperature decreases. Note that the parameters of the figure have been chosen to be in rough agreement with those describing the situation in the glass-forming systems: There is a factor of two between the largest and the smallest temperatures, and the intermediate one corresponds to a microscopic value of the characteristic decay length of  $Q(L)$ ,  $\xi_b/2 = 1$  lattice spacing.

Taking advantage of the exact result for  $Q_c(L)$ , the numerical data analysis developed in Ref. 1 can be repeated, by fitting a coarsely sampled  $Q_c(L)$  in its nonexponential regime to a compressed exponential law

$$Q_c(L) \simeq A \exp[-(L/\xi)^\zeta]. \quad (11)$$

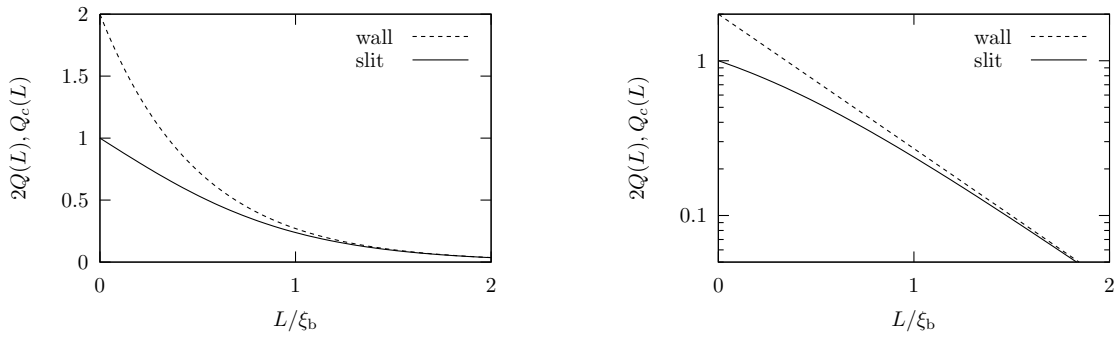


FIG. 1. Linear and semi-log plots of the spin overlaps of the one-dimensional Ising model in the “wall” and “slit” geometries. The distances are scaled by the bulk correlation length  $\xi_b$ .

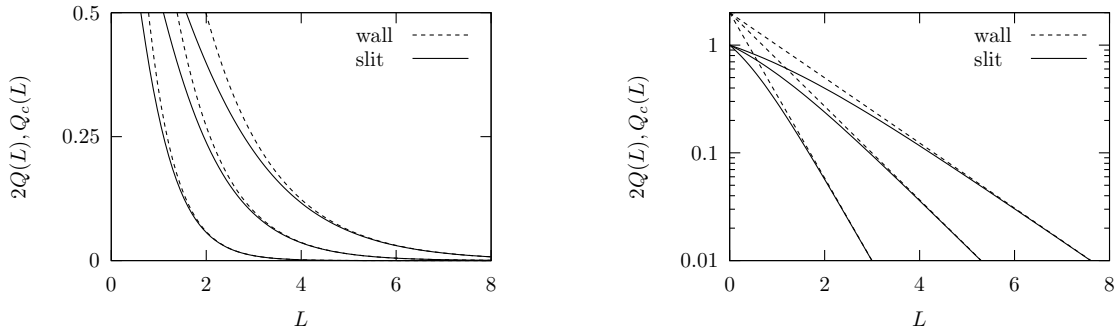


FIG. 2. Linear and semi-log plots of the spin overlaps of the one-dimensional Ising model in the “wall” and “slit” geometries at different temperatures. From left to right,  $T = \beta^{-1} = 1.6T_0, T_0, 0.8T_0$ , where  $T_0 \simeq 1.42J$  is such that the bulk correlation length  $\xi_b(T_0) = 2$ .

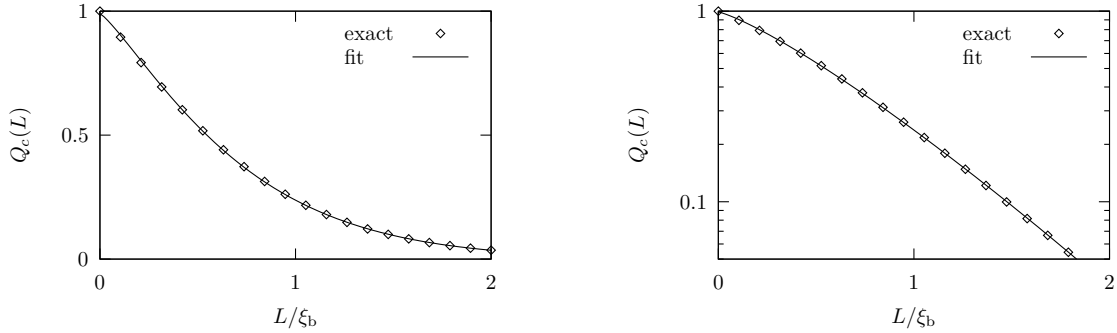


FIG. 3. Linear and semi-log plots of the discretely sampled spin overlap of the one-dimensional Ising model in the “slit” geometry and its best fit by a compressed exponential law on the domain  $0 \leq L/\xi_b \leq 2$ . The distances are scaled by the bulk correlation length  $\xi_b$ .

As seen in Fig. 3, an excellent fit is obtained with a moderate anomalous exponent  $\zeta \simeq 1.22$  and an effective decay length  $\xi \simeq 0.75\xi_b$ , larger than the actual one which is the same as in the wall geometry and equal to  $\xi_b/2$ .

Interestingly, in the study of glass-forming liquids in the slit geometry, a crossover from a high-temperature exponential to a low-temperature nonexponential behav-

ior, associated with numerically-determined larger correlation lengths than in the wall geometry, is similarly observed, but with larger and temperature-dependent anomalous exponents and lengthscale ratios. In this context, it is interpreted as a signature of glassiness. This obviously does not apply to the present model, in which the somewhat weaker quantitative effects might be the mere consequences of its rather impoverished physics.